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Engineered Nano-bio Hybrid Electronic Platform for Solar Energy Harvesting

by Shashi P. Karna, Govind Mallick, Mark H. Griep, and Craig R. Friedrich

ARL-TR-5226 **June 2010**

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14. ABSTRACT
Bacteriorhodopsin is an opto-electric protein found in the membrane of the extremophile bacterium *Halobacterium salinarum*. The protein creates a charge gradient across its 6-nm thickness and, when integrated with inorganic electron generation and transport materials such as titania nanotubes, may be useful as a new class of photon harvesters. Bacteriorhodopsin strongly absorbs light near the 570-nm wavelength, but its photoelectric activity is now shown to increase by at least 35% when integrated with ultraviolet (UV)-scavenging quantum dots. We also investigated several solar cell architectures by integrating the protein with various conductive substrates of indium tin oxide, zinc oxide, and titanium dioxide nanotubes. Electrolytes tested included physiological phosphate buffer and an iodine-triiodide material used in dye sensitized solar cells. Preliminary results from millimeter-scale test devices show voltage and current levels of potential use in microelectronic devices.

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Bio-nano hybrid, bacteriorhodopsin, quantum dot, titania nanotube, solar cell

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1. Objective

The Future Force (FF) Soldier will be equipped with a wide array of new technology, all requiring electrical power for operation. It will be critical to incorporate energy harvesting systems into the Soldier's gear to accommodate the power demands and lessen the dependence on cumbersome batteries. Photovoltaic (PV) technology is one such option, but is currently impractical due to its high cost and low efficiency, and implementation barriers. The evolutionary development of biological systems (for this research, the optical protein bacteriorhodopsin [bR], which is an opto-electric protein found in the membrane of the extremophile bacterium *Halobacterium salinarum*) has created natural and sustainable nanoscale materials with capabilities beyond that of current technology, including a wider absorbance spectrum. Integrating this biological material with inorganics, including semiconductor quantum dots (QDs) and titanium dioxide nanotubes (NTs), opens new possibilities for protein sensitized solar cells (PSSC). The objective of this research is to better understand the mechanism of efficient photocurrent generation in bio-nano hybrid PSSC material for use in photovoltaic applications.

2. Approach

Structurally similar to the visual rhodopsin found in the mammalian eye, bR has a wide spectral absorbance and most strongly absorbs visible light in the 570-nm spectral region, as shown in figure 1a. With the absorbed photonic energy, the protein's retinal undergoes an isomerization and initiates proton pumping across the 5.5-nm-thick protein. Studies have demonstrated that bR can create a constant current output upon illumination, as shown in figure 1b.

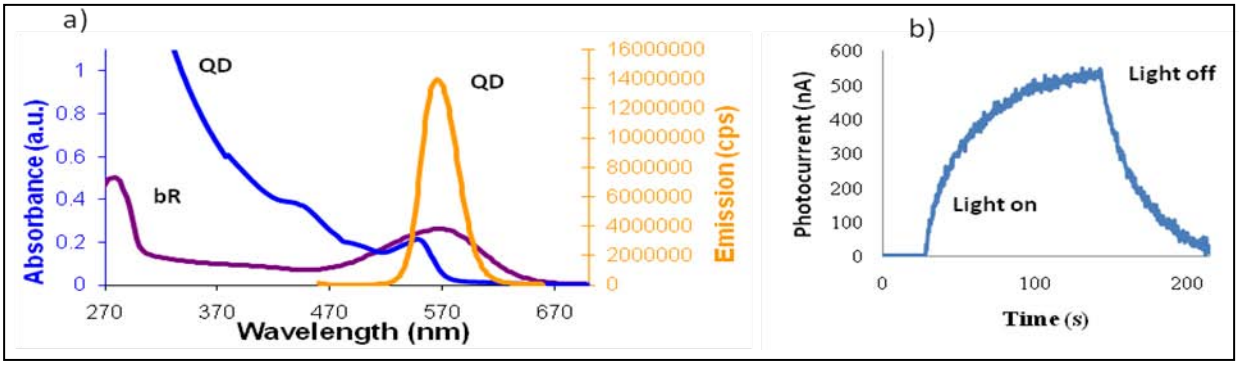

Figure 1. (a) QD absorbance (blue) and emission (orange) properties of QDs and absorbance (purple) of bR; and (b) the photocurrent generated from six oriented monolayers of bR.

Previous research has theorized the utility of bR in PV applications, calculating bR's maximal theoretical light-harvesting efficiency to be 25% and its average specific power as 2,103 W/kg, compared to only 18% and 32 W/kg, respectively, for silicon (*1*). Preliminary studies show (figure 1a) that the addition of QDs into the bR PV system greatly extends its absorptive capabilities into the ultraviolet (UV) and shorter wavelength visible range. The QDs can be engineered to re-emit the absorbed light at the wavelength that is most efficiently absorbed by bR, thus increasing the amount of solar energy harvested. In mammalian rhodopsin, the photon bleached retinal (a vitamin A derivative) is expelled from the protein, requiring a supply of fresh retinal from the host. bR does not expel the retinal but instead catalyzes it back to the unbleached form making it a more adaptable photo material.

Tests conducted by Griep et al. (*2–4*) showed an increase in the photoelectric response of bR due to photon scavenging of bound semiconductor QDs. Figure 2a shows the increase in fluorescence between just bR and bR with attached QDs to confirm the linkage. Figure 2b shows an ~35% increase in the bR/QD photovoltage over that of just bR. This confirms that QDs play an important role in enhancing the electrical output of the bR in a photon scavenging system. With this evidence, the current work has focused on integrating bR with one-dimensional (1-D) nanostructures, a necessary next step in understanding the contributions of incremental advances in a bio-nano-hybrid photon harvester.

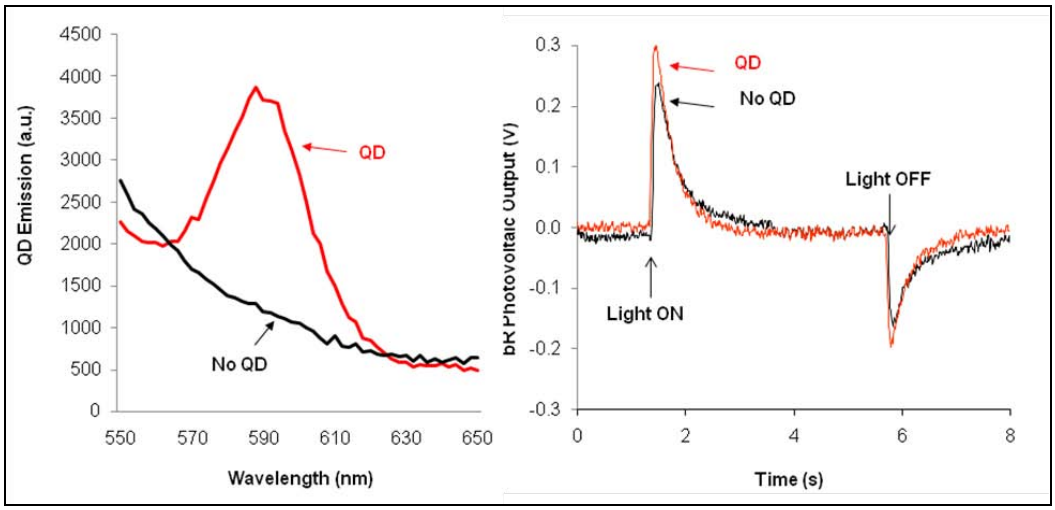

Figure 2. Attachment of QDs to bR is confirmed by the large increase of fluorescence upon UV illumination (left). The QD fluorescence and resonance energy transfer to the bR increases the photovoltage by ~35% (right).

Research was conducted (*4*) that quantified the relative influence of chemically attached QDs on bR absorption. It was determined that QDs will effectively absorb light at short solar wavelengths and re-emit that light allowing the bR to use it in its native charge separation process. This is in addition to the fact that bR has a relatively broad absorption spectrum

compared to narrow wavelength absorption/conversion of inorganic materials because of bandgap matching.

The bR PSSC has an advantage over a dye sensitized solar cell (DSSC) in the way in which charge is moved. bR is most often used in the form of native cell membrane patches containing many bR monomers. The membrane patches (termed purple membrane [PM]) have a charge differential across the sides of the membrane at neutral pH. Thus, the PM can be oriented and deposited in an electric field, which results in the charge being directed vectorally into the underlying substrate. However, because the bR pumps a proton, this fact may have applicability in helping maintain an adequate supply of "holes" at the bR/electrolyte interface to inhibit exciton recombination. Additionally, the bR pumps a proton (hole) each 10 ms and replaces that proton from the aqueous electrolyte, freeing an electron. This is a directed chemical process so the probability of the electron-proton recombination may be reduced.

For the current PSSC, titania (TiO_2) NTs were investigated as the 1-D electron transport substrate (*5*). TiO_2 NTs were synthesized by anodization of bulk high purity titanium (Ti) foils and Ti6Al4V alloy foils, and into thin-film Ti evaporated onto substrates including indium tin oxide (ITO). ITO is both transparent and electrically conductive and could serve as one or both electrodes in the PSSC, especially since TiO_2 NTs can be made transparent. This could potentially double the capacity of the PSSC by having two bR/substrate assemblies per cell, connected either in series or parallel depending on the individual orientation of the PM on each.

3. Results

The TiO_2 NTs were electrochemically etched in a solution of ammonium fluoride (NH_4F) in ethylene glycol and water at 60 VDC. Figure 3 shows the resulting structures in bulk Ti foils and figure 4 is in evaporated thin-film Ti on ITO-glass. As these figures show, the fabrication of TiO_2 NTs can be accomplished in bulk Ti foil and micron-thick Ti sputtered onto other material substrates. This provides initial results showing that TiO2 PSSCs might be fabricated onto a variety of rigid or flexible, thin and lightweight substrates.

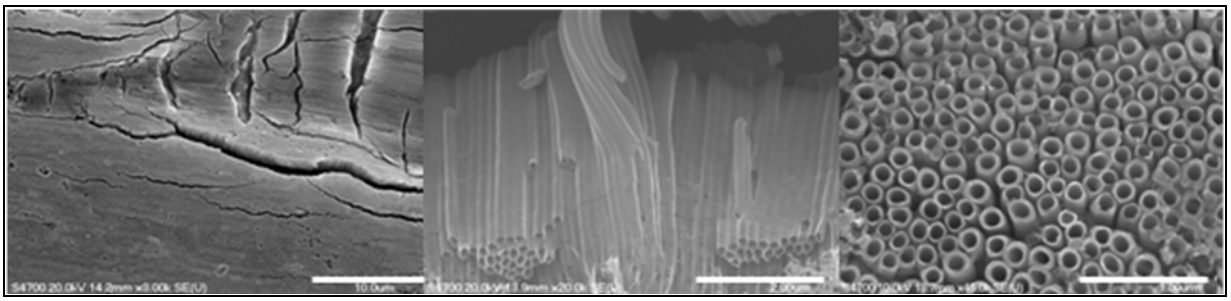

Figure 3. TiO_2 NTs etched in bulk Ti foils with 0.2 Wt% NH_4F at 60 VDC for 2 h. The scale bars are 50 μm (left), 2 μm (center), and 1 μm (right) (*5*).

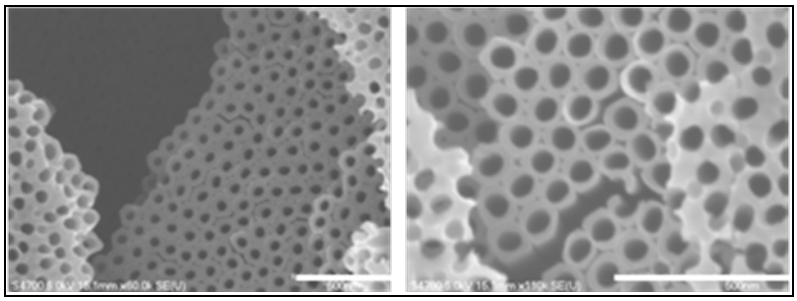

Figure 4. TiO_2 NTs etched in 2-μm-thick sputtered Ti on ITO with 0.2 Wt% NH_4Fat 60 VDC for 2 h. The scale bars are 500 nm (left) and 500 nm (right) (*5*).

Figure 5 shows a substrate architecture composed of loosely bound TiO_2 nanotubes or zinc oxide (ZnO) nanowires on ITO-glass, coated with an oriented layer of bR of unknown thickness (estimates are approximately 20 μm) (*6*). The assembly was immersed in 0.1 M potassium chloride (KCl) electrolyte as an electrochemical cell with transient voltages recorded.

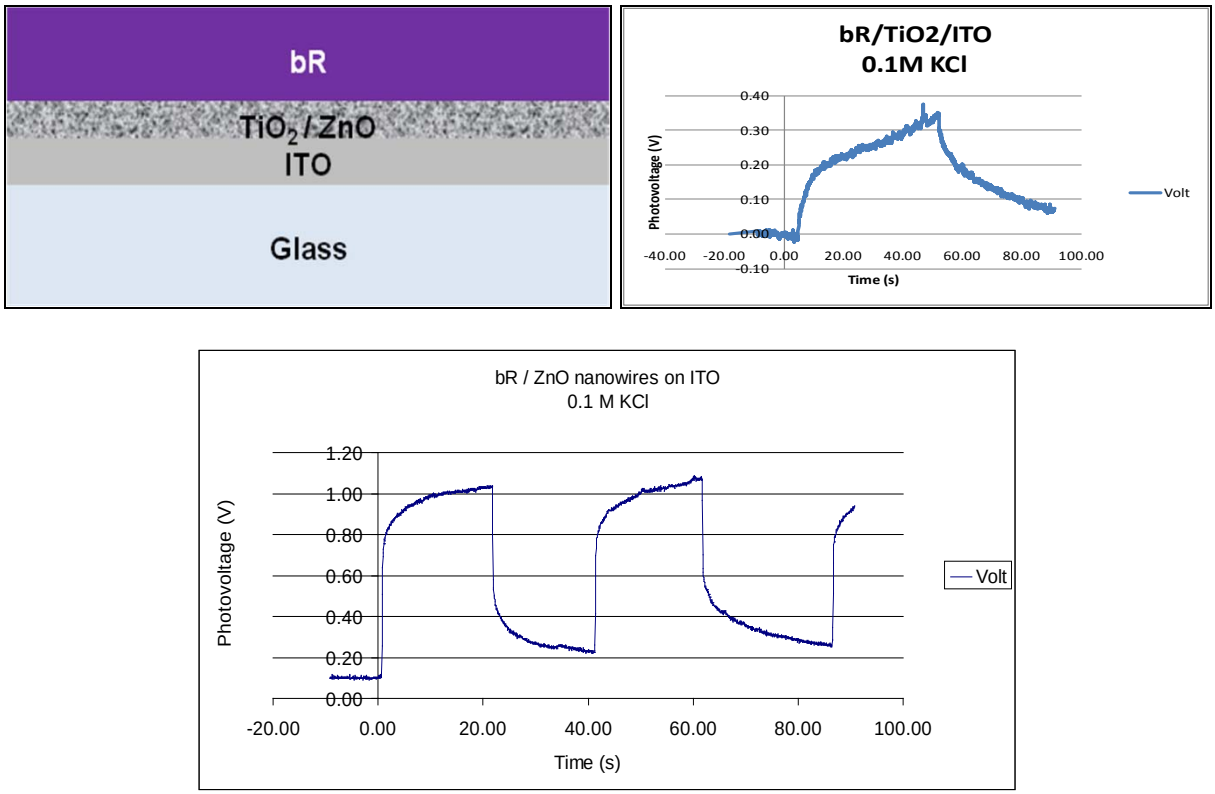

Figure 5. Architecture and preliminary results of PSSC of TiO_2 NTs (upper left) showing voltage output of 35 mV (plot shows output through 10× isolation amplifier) and ZnO nanowires (bottom) showing light cycling and 100 mV output (plot shows output through 10× isolation amplifier) (*6*).

Bacteriorhodopsin was oriented and deposited onto ITO glass without an underlying 1-D material. This was performed to investigate the effect of an electrolyte commonly used in DSSCs, that electrolyte being an iodine/tri-iodide solution. The architecture and preliminary

result are shown in figure 6. Here, the output is not magnified and shows ~600 mV of output. One preliminary test (not shown here) resulted in a current output of approximately 0.8 μA with an active area 5 mm in diameter. Conventional solar calculator cells provide approximately 0.2 μA of current with a much larger active area.

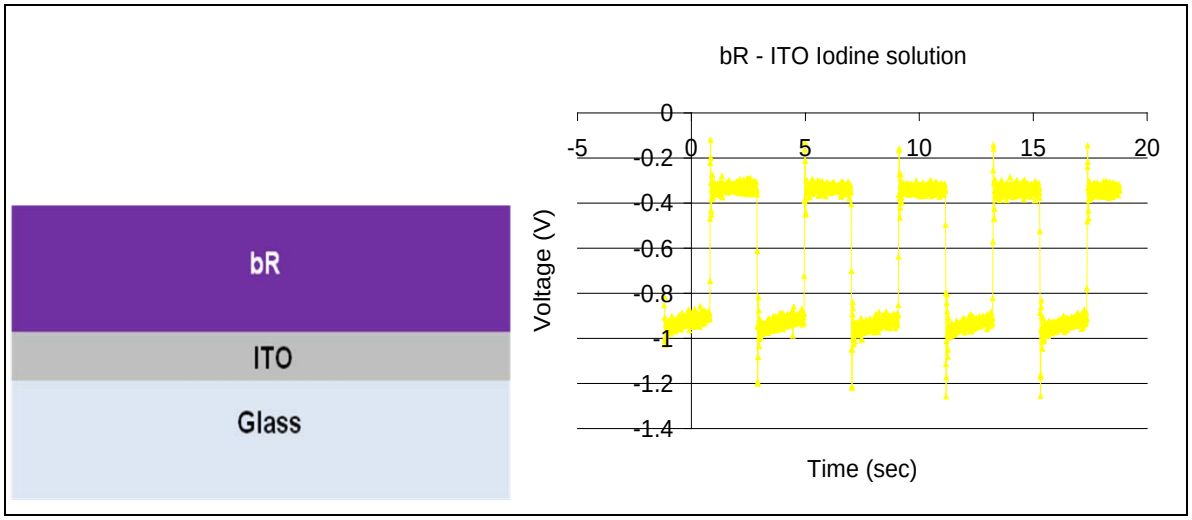

Figure 6. Output of bR/ITO-glass photon harvester in electrochemical cell and iodine/tri-iodide electrolyte solution (*6*).

4. Conclusions

The first-year work, building upon prior results, has shown that the photovoltage output of bR is enhanced with the integration of semiconductor QDs attached via the biotin-streptavidin linkage. This represents the first incremental improvement in increasing photon-to-electrical transduction in the bio-nano hybrid. Building upon this, substrates of 1-D TiO_2 NTs were fabricated in bulk and thin-film material with "green" chemistry, and in a relatively short time, for use as the carrier generating medium for our nano-bio hybrid solar cell platform. This process can be easily scaled up to industrial production and adapted to substrates with arbitrary shape. Using the 1-D TiO_2 NTs and bR, we showed that with oriented bR, the nano-bio hybrid platform performs as an effective photon harvester. Results are still preliminary and the various efficiency metrics have not yet been determined; however, the initial set of results appears to be encouraging. The next incremental step will be to investigate gel-type electrolytes that do not degrade the bR protein. Additional work will study the temporal stability of simple bR solar cells under extended periods of activity and diurnal light cycling.

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6. Transitions

This work will be continued in the second-year Director’s Research Imitative (DRI) for further development.

List of Symbols, Abbreviations, and Acronyms

1-D	one-dimensional
ARL	U.S. Army Research Laboratory
bR	bacteriorhodopsin
DRI	Director's Research Initiative
DSSC	dye sensitized solar cell
FF	Future Force
ITO	indium tin oxide
NTs	nanotubes
PM	purple membrane
PSSC	protein sensitized solar cells
PV	photovoltaic
QDs	quantum dots
Ti	titanium
TiO_2	titanium dioxide or titania
UV	ultraviolet
ZnO	zinc oxide

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